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REMARKS

This Amendment rewrites claims 1, 25 and 26. Claims 1-7, 9-15, 20, 21, 23 and 25-27 are pending.

Examiner Lee is thanked for allowing claims 20, 21, 23 and 27. It is believed this Amendment places the entire application in condition for allowance for the reasons which follow.

Examiner Lee is also thanked for the courtesies extended to the undersigned during a personal interview held January 6, 2004 as well as a telephonic discussion held March 3, 2004. The Examiner Interview Summary Record accurately reflects the substance of the personal interview. The March 3, 2004 telephonic discussions concerned a draft Rule 132 Declaration. No agreement was reached during these telephonic discussions.

Entry of this Amendment is earnestly requested, as it is believed to (1) place the application in condition for allowance, (2) not to raise any new issue or require further search by the Examiner, (3) to be directly responsive to the telephonic discussions held March 3, 2004 and (4) to place the application in even better form for appeal, should such appeal be necessary. More particularly, this Amendment amends each of claims 1, 25 and 26 by deleting the phrase "and where at least one of R¹, R², R³, R⁴, R⁷ and

R⁸ is not hydrogen". This amendment was made in response to the Examiner's objection that this phrase creates an ambiguity with respect to the proviso in those claims requiring that at least one of R⁷ and R⁸ is not hydrogen.

The 35 U.S.C. § 103(a) rejection of claims 1-7, 9-12, 25 and 26 over PCT Patent Publication WO 98/22486 to Ewen et al. is respectfully traversed. Process claims 1-7 and 9-12 are directed to the preparation of ethylene polymers using a catalyst system formed by contacting a substituted¹ metallocene compound of formula (I) with a compound selected from a Markush group consisting of an alumoxane and a compound capable of forming an alkyl metallocene cation. The inventors have discovered that the use of a specified halogen-containing metallocene catalyst with substitution at either or both of the R⁷ and R⁸ positions permits unexpectedly high production of high molecular weight polyethylene.

These surprising results are demonstrated in Table 1. Compounds Z_s-0 (Example 3), Z_s-1 (Example 4), Z_s-2 (Example 7) and Z_s-3 (Examples 5 and 6) each have at least one of R⁷ and R⁸ which is not hydrogen. These compounds have higher catalytic activity and I.V. than compounds Z_s-51 (Example 1) and Z_s-50 (Example 8) which

¹At least one of R⁷ and R⁸ is not hydrogen.

are not substituted at either the R⁷ or R⁸ position. Moreover, the data for Examples 5 and 6 can be compared to Example 1. The Examiner's attention is directed to the attached Rule 132 Declaration by Dr. Tiziano Dall'Occo. The Declaration is based on the draft 132 Declaration submitted to the Examiner, and was revised to address the Examiner's hopeful comments thereon. Reconsideration and withdrawal of the obviousness rejection of claims 1-7, 9-12, 25 and 26 over Ewen et al. is respectfully requested.

The 35 U.S.C. § 103(a) rejection of claims 13-15 over Ewen et al. in view of U.S. Patent No. 5,948,873 to Santi et al. is respectfully traversed. These claims all depend from claim 1, and thus are patentable over Ewen et al. for at least the same reasons as claim 1.

Applicants have previously pointed out that one of ordinary skill in the art would not combine Ewen et al. with Santi et al. because the secondary reference discloses a different class of metallocenes. It is even more apparent that Santi et al. fails to disclose or suggest that the metallocene compounds of the claimed process exhibit significantly higher activity and produce

polyethylene of higher molecular weight than suggested by Ewen et al. when used to polymerize propylene.

Reconsideration and withdrawal of the obviousness rejection of claims 13-15 over Ewen et al. in view of Santi et al. are earnestly requested.

It is believed this application is in condition for allowance. Reconsideration and withdrawal of all objections and rejections of claims 1-7, 9-21 and 23-27, and issuance of a Notice of Allowance directed to claims 1-7, 9-15, 20, 21, 23 and 25-27, are earnestly requested. The Examiner is requested to telephone the undersigned should he believe any further action is required for allowance.

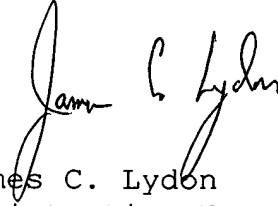
A Petition and fee for a three month Extension of Time are attached. It is not believed that any additional fee is required for entry and consideration of this Amendment. Nevertheless, the

U.S. Patent Appln. S.N. 09/914,305
AMENDMENT AFTER FINAL REJECTION

PATENT

Commissioner is hereby authorized to charge our Deposit Account 50-1258 in the amount of any such required fee.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "James C. Lydon". The signature is fluid and cursive, with the first name "James" and last name "Lydon" clearly distinguishable.

James C. Lydon
Registration No. 30,082

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Enclosures:

Petition for Extension of Time
Rule 132 Declaration

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NR. 3982 P. 2



US 18024

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent application of:

Tiziano Dall'occo et al.

Serial No.: 09/914,305

Filed: August 27, 2001

For: **PROCESS FOR THE PREPARATION
OF ETHYLENE POLYMERS**

Examiner: Rip Lee

Art Unit: 1713

March 20, 2004

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450**RULE 132 DECLARATION**

I, Dr. Tiziano Dall'Occo hereby declare that:

1. I am Tiziano Dall'Occo.
2. THAT in 1981 I received a Degree in Chemistry at the University of Ferrara, faculty of Science.
3. THAT in 1983-84 I spent two years at the University of Ferrara in the organic synthesis as a Fellow of P.R.D. courses. In November 1984 I was employed by Dutral S.p.A. (Montedison group) at the "G. Natta Research Center" in Ferrara as a researcher in the Ziegler-Natta polymerization catalysis applied to the synthesis of polyethylene and ethylene copolymers. In 1989 I joined HIMONT ITALIA S.r.l. in their "G. Natta Research Center" where I worked as project leader of basic research in the study of catalytic systems for ethylene

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NR. 3982 P. 3

homo- and copolymerization. My present position in Basell Polyolefine Italia S.p.A. is Scientist in olefin polymerization catalysis.

4 That I have co-authored at least 25 papers on various aspects of inorganic and organic chemistry and olefin-polymerization, and that I am co-inventor of 26 patent applications relating to olefin copolymerization by Ziegler-Natta based catalyst including the use of metallocene based systems.

5. THAT I am one of the inventors and familiar with the disclosure and the claims of the above-identified application Serial No 09/914,305.

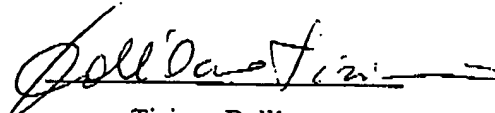
6. THAT I understand the Examiner has questioned whether the three-fold activity improvement of Example 3 over Comparative Example 8 would be unexpected to one skilled in the art. My answer is that this improvement is unexpected and surprising because the references of record in this application are silent with respect to any activity improvement which might result from changing from the catalyst of Comparative Example 8 to the catalyst of Example 3 for the polymerization of ethylene polymers.

7. THAT I understand the Examiner has also questioned whether Examples 5 and 6 can be compared to the known compound of Example 1 in view of the difference in Al/Zr ratio (3000 for the known compound of Example 1 vs. 1000 and 1060, for Examples 5 and 6 respectively, and because reaction times were not held constant. My answer is that these Examples can be directly compared because one skilled in the art would recognize that at least up to values of about 2000, higher Al/Zr ratios result in higher activity values, so that based on differences in the Al/Zr ratio, the known compound of Example 1 would have been expected to exhibit higher activity values than Examples 5 and 6, see Figure 1 of Deffieux

et al., Activation Of MAO: Activity Of Metallocene Catalysts With Low MAO Content For Olefin Polymerization, published in Metallocenes '95, April 1995, copy attached hereto. Moreover, the activity measurement (Kg/g Zr.h) shown in Table 1 of the specification takes into account differences in the amount of metallocene used and the length of reaction. Thus, a comparison of the activity measurement of Examples 5 and 6 to the known compound of Example 1 is valid.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and that further these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the present application or any patent resulting therefrom.

Signed this 20th day of March, 2004


Tiziano Dall'occo

I hereby certify that this correspondence is being deposited with sufficient postage thereon with the United States Postal Service as first class mail in an envelope addressed to: Commissioner for Patents
P.O. Box 1450, Alexandria, VA 22313-1450 on March 20, 2004.

3/18/2004

Date of Signature

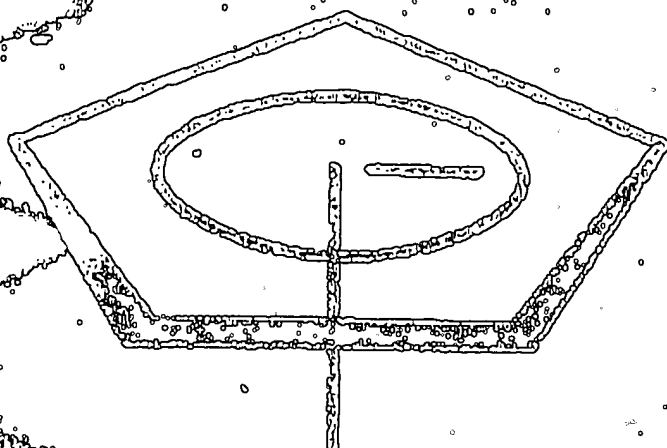
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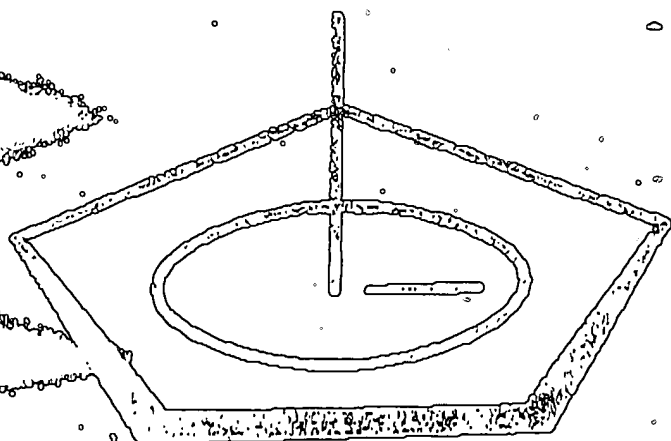
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International Congress on Metallocene Polymers

26 - 27 April 1995
Brussels, Belgium



Metallocenes '95



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ACTIVATION OF MAO : ACTIVITY OF METALLOCENE CATALYSTS WITH LOW MAO CONTENT FOR OLEFIN POLYMERIZATION

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INTRODUCTION

Since the discovery of the powerful combination of Metallocenes (IVB group) with Methylaluminoxane (MAO) as catalytic systems for olefin polymerizations¹⁻⁷, much efforts have been paid to establish the nature of the active catalytic species and their mechanism of formation.

The complexity of the MAO structure, which may moreover drastically vary with its preparation mode⁸⁻¹⁰, the very large proportion of co-catalyst required with respect to the metallocene to get an optimal catalytic activity¹¹, the presence of trimethyl aluminium in equilibrium with MAO, as unavoidable side co-catalyst component, still put some shadow on the various elementary steps which lead to the formation of the metallocene active species in the MAO-based systems¹²⁻¹³.

Besides, researches to by-pass the difficulties associated to the MAO cocatalyst, in particular the serious drawback for industry resulting from the very large amount of aluminoxane needed for metallocene activation, have led to the development of MAO-free metallocene catalysts¹⁵⁻¹⁸. Among the different routes explored, the use of non coordinating anions such as $B(C_6F_5)_4^-$ as substitutes of MAO has been very successful. Moreover, structural and mechanistic studies performed with these systems have confirmed that cationic metallocene complexes are the catalytically active species in the polymerization of α -olefins. It has been shown that the latter species can be generated from dialkylmetallocene, by protolysis with weakly acidic ammonium salts or by alkyl abstraction with triphenylcarbenium salts.

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It is now admitted that similar cationic species are also formed from metallocene dichloride in the presence of methyl aluminoxane/trimethyl aluminium as co-catalytic system. The latter should first alkylate or dialkylate the dichlorometallocene compound. Then interactions of MAO with the new alkylated metallocene species are supposed to generate the alkylated metallocenium ion.

Aluminoxanes have also the important role to scavenge the impurities.

The various reaction parameters which may influence the co-catalytic efficiency of MAO in the metallocene activation process for olefin polymerization have been investigated. This study was performed in the case of a model system¹⁹⁻²¹, i.e., hex-1-ene polymerization in the presence of *rac*-ethylene-bis-Indenyl zirconium dichloride/MAO as catalyst. An extension of these results to ethylene polymerization is also presented.

EXPERIMENTAL

Materials :

rac-Et-Ind₂ZrCl₂ and MAO (10 or 30% in toluene) from Witco were used as received.

Toluene, heptane and hex-1-ene were dried on Na/benzophenone, distilled and stored under dry nitrogen.

Methylene dichloride was dried in the presence of a small amount of triethylaluminium, distilled and stored under nitrogen.

Isododecane and Ethylene were dried over two columns of molecular sieves (4 Å and 13X).

Polymerization and kinetic procedures.

Hex-1-ene polymerization : *rac*-Et-Ind₂ZrCl₂ ($\sim 10^{-6}$ mole) was first introduced under dry nitrogen in the dilatometer chamber (volume 15 ml) and vacuum dried. A solution of MAO and hex-1-ene in the polymerization solvent, thermostated at 20°C, was then introduced under nitrogen through a canula into the dilatometer.

Kinetics of polymerization were immediately followed by recording the volume contraction of the polymerization solution in the dilatometer.

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Polymerization of hex-1-ene with catalyst preformation : For polymerization experiments performed in the presence of a preactivated catalyst, the metallocene was first mixed in the dilatometer chamber with a solution of MAO in the activation solvent (generally CH_2Cl_2 , 1ml). Then after a given reaction time (2 to 30 min), 14ml of the monomer solution in the polymerization solvent, containing a small amount of trihexylaluminium as drying agent, was introduced in the dilatometer and polymerization kinetics were immediately recorded.

Polyhexene molar masses were measured by size exclusion chromatography on the basis of polystyrene calibration.

Ethylene polymerization : A solution of MAO into a small volume (about 6 ml) of either the polymerization or the pre-activation solvent was added to the metallocene. The catalyst mixture was then introduced into the polymerization reactor containing the solvent (500ml), a small amount of triethylaluminium as drying agent and ethylene ($P=5$ bars). The polymerization was recorded by following the ethylene pressure drop. The use of an ethylene reservoir allowed to keep the pressure drop to less than 5% and therefore to neglect the effect of this variable on kinetics²².

RESULTS AND DISCUSSION

Polymerization of hex-1-ene with *rac*-Et-Ind₂ZrCl₂/MAO

Hex-1-ene polymerization was investigated, at 20°C, in different reaction media, with the *rac*-Et-Ind₂ZrCl₂/MAO catalytic system. Kinetics of hex-1-ene conversion were followed by dilatometry.

a) Polymerization in toluene

The influence of the relative proportion of MAO on the catalytic activity of *rac*-Et-Ind₂ZrCl₂ (Kg PHex/mole Zr.h.[Hex]), in toluene, is presented on Figure 1. In agreement with literature data¹⁹, the activity increases with the MAO/metallocene ratio and becomes maximal for ratio in the range $2-4 \cdot 10^3$.

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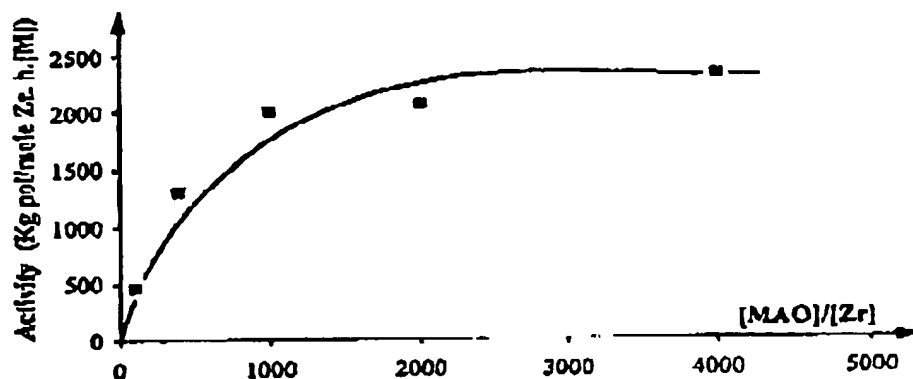


Figure 1 : influence of the MAO/Zr ratio on the hex-1-ene polymerization in toluene : $[Zr] = 5 \cdot 10^{-5} \text{ M}$; $T = 20^\circ \text{C}$; $[Hex] = 1 \text{ M}$.

The Logarithmic variations of the polymerization rate with time for different MAO/Zr ratio (100, 400, 4000) are presented in Figure 2. As may be seen a linear relationship is observed from the initial stage up to very high monomer conversions (>80-90%). Besides the first order dependance of the polymerization with respect to hex-1-ene, this indicates that active species rapidly form and remain at constant concentration during the whole polymerization.

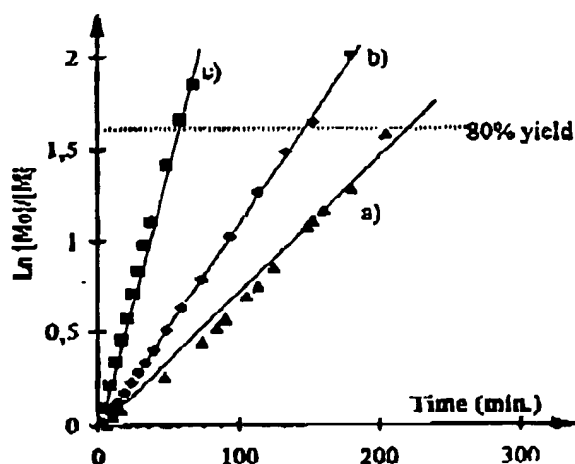


Figure 2: Semi-logarithmic variations of hex-1-ene concentration versus polymerization time : solvent toluene ; $[Zr] = 5 \cdot 10^{-5} \text{ M}$; $T = 20^\circ \text{C}$; $[Hex] = 1 \text{ M}$; MAO/Zr : a) 100 ; b) 400 ; c) 4000

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The stability of active species was further confirmed by adding on the same catalytic system a fresh feed of monomer, after the initial charge had been completely polymerized. As shown in Figure 3, throughout the two-stages polymerization, the rate of polymerization remains almost constant (less than 10% decrease) in agreement with the presence of very long-lived active species.

Despite the stability of active species, poly(hex-1-ene) molar masses, do not significantly vary neither with the initial monomer concentration and the amount of monomer consumed, nor with the amount of MAO present, suggesting that the polymer chain length ($\bar{M}_w \approx 4 \cdot 10^4$, $I \approx 2$) is controlled by unimolecular transfer.

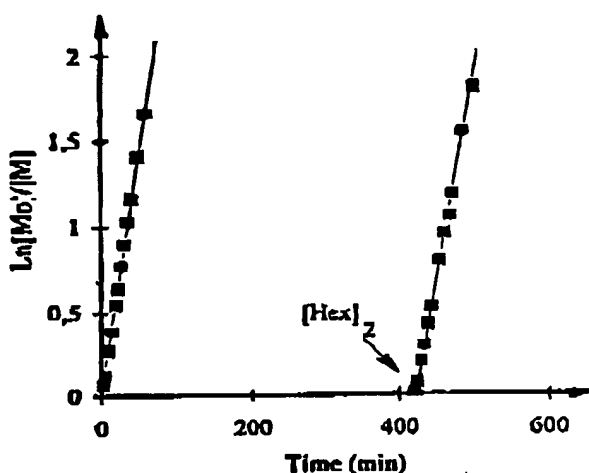


Figure 3: Semi-logarithmic variations of hex-1-ene conversion versus polymerization time for two monomer feeds : solvent toluene ; $[Zr] = 5 \cdot 10^{-5} M$; $T = 20^{\circ}C$; $[Hex]_1 = 1M$; $[Hex]_2 = 0,5M$; $MAO/Zr = 4000$

These results strongly suggest that, in given experimental conditions, the polymerization activity reflect the proportion of active species formed with respect to initial *rac*-Et-Ind₂ZrCl₂, the latter being directly dependant on the amount of MAO. According to this interpretation, for MAO/Zr ratios of 400 and 100 the proportion of active species formed would be respectively only 35% and 20% of those formed with a ratio MAO/Zr of 4000.

These conclusions led us to investigate the role of the reacting media on the rate of formation of active species.

b) Polymerization in methylene dichloride

The postulated cationic nature of the active metallocene complexes^{13,17} led us to investigate the effect of reacting media of higher polarity. Methylene dichloride was selected for this study because of its drastic influence on the dissociation equilibrium of carbocationic species in cationic polymerization and its limited influence on the reactivity of propagating active species. This behavior can be attributed both to a polarity effect and to the low coordinating power of the CH_2Cl_2 molecule. Several studies dealing with the use of methylene dichloride for propene^{23,24} and styrene²⁵ polymerizations with metallocene catalysts have been reported. In most cases, high MAO/metallocene ratio (>1000) were used and no significant positive effect of the polar medium on the catalyst activity was observed. Moreover, side reactions leading to a decrease of the stereospecificity of polypropylene or to the formation of atactic polystyrene were noticed. A significant enhancement of the propylene polymerization rate was noticed however in methylene dichloride in the case of the system $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)_2/\text{Al}(\text{CH}_3)_3\text{-Al}(\text{CH}_3)_2$.²⁴

The influence of the proportion of MAO/Zr on the catalytic activity of *rac*- $\text{Et-Ind}_2\text{ZrCl}_2$ towards hex-1-ene polymerization, in CH_2Cl_2 , is presented on Figure 4. As may be seen, the activity sharply increases with the MAO/metallocene ratio and rapidly reaches a maximum for proportions of MAO/Zr of 200, a much lower value than for polymerization in toluene. Moreover, the maximal activity at the plateau is higher in CH_2Cl_2 than in toluene.

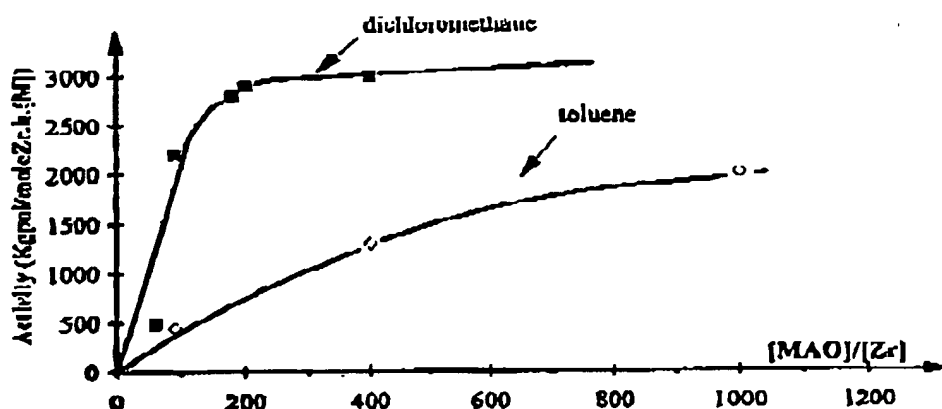


Figure 4 : influence of the MAO/Zr ratio on hex-1-ene polymerization in methylene dichloride : $[\text{Zr}] = 5 \cdot 10^{-5} \text{ M}$; $T = 20^\circ\text{C}$; $[\text{Hex}] = 1 \text{ M}$.

The Logarithmic variations of the polymerization rate with time for two different MAO/Zr ratio (100, 400), presented in Figure 5, is again rectilinear during the whole polymerization (>80-90%). This indicates that in methylene dichloride too, active species rapidly form and remain at constant concentration, as previously noticed in the aromatic solvent

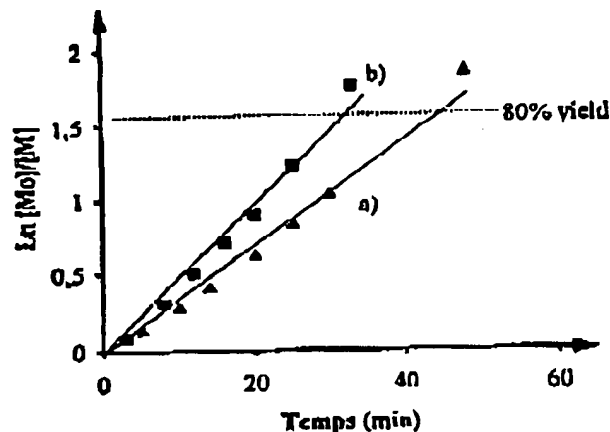


Figure 5: Semi-logarithmic variations of hex-1-ene concentration versus polymerization time in CH_2Cl_2 : $[\text{Zr}] = 5 \cdot 10^{-5} \text{ M}$; $T = 20^\circ\text{C}$, $[\text{Hex}] = 1 \text{ M}$; MAO/Zr: a) 100, b) 400

As reported for toluene, poly(hex-1-ene)s molar masses, do not significantly vary with the amount of MAO; the polymer chain lengths are however lower in methylene dichloride by a factor of about 2 ($\overline{M}_w \approx 2 \cdot 10^4$, $I \approx 7$), indicating that the spontaneous transfer constant, likely through β -hydride abstraction, increases more with dielectric constant than the propagation rate constant. It is worthy to mention that the isotacticity of the poly(hex-1-ene)s remains high and apparently does not noticeably changed with the polymerization solvent.

The catalytic activity observed at MAO/Zr ratio of 100 is about 70% of the one observed for 400. However, for ratio lower than 100, the catalytic activity drastically decreases. Since the concentration of aluminoxane used in these conditions became quite low, a possible deactivation due to impurities was suspected: the latter might not be completely scavenged by MAO, or a large fraction of the co-catalyst could serve as cleaning agent. To investigate these possible effects, a series of polymerization experiments were implemented with an

aluminumoxane concentration maintained in the range $5\text{-}20 \cdot 10^{-3}$, corresponding approximately to the one previously used for ratio MAO/Zr of 200-400, and the metallocene concentration was increased, to reduce the proportion of the co-catalyst with respect to the metallocene from 100 to 10

Results collected in Figure 6 show that the catalytic activity of the metallocene (expressed in Kgpol/mole Zr.h.[M]) is still maintained at about 60 % of the plateau value for MAO/Zr ratio as low as 30. Again in these conditions, on the basis of the polymerization kinetic profile, we may consider that the catalytic active species rapidly form and that their concentration remains constant during the whole polymerization.

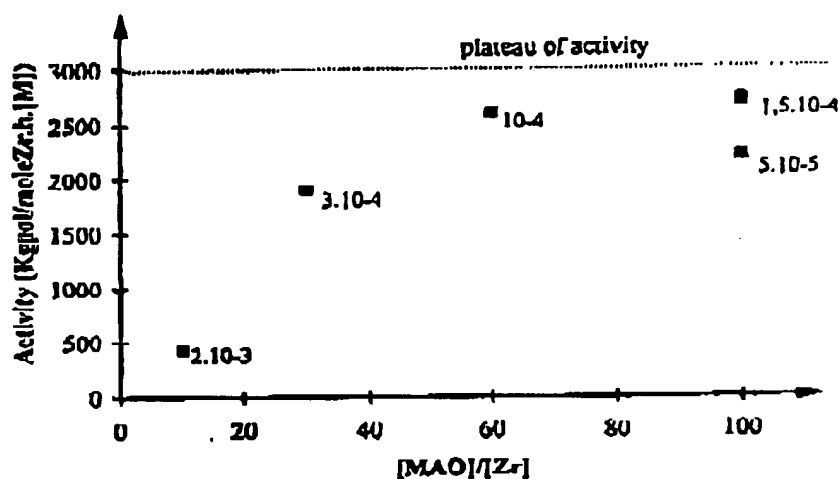


Figure 6 : influence of the MAO/Zr ratio (low range) on hex-1-ene polymerization in methylene dichloride ; [Zr] in M given in the figure ; [MAO] = $20\text{-}5 \cdot 10^{-3}$ M ; $t = 20^{\circ}\text{C}$; [Hex] = 1 M ;

These results emphasize the determining role of the reacting media at the initial stage of the formation of catalytically active metallocene species. This led us to investigate the possibility to preactivate the metallocene/ MAO systems in appropriate solvent conditions.

c) Preactivation of the catalytic system in methylene dichloride

In order to take benefit of the positive effect of CH_2Cl_2 in the formation of catalyst species, a series of experiments was implemented in which the catalyst was preformed in the chlorinated solvent. Hex-1-ene polymerization were then

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performed in toluene or heptane. For a same concentration in *rac*-Et-Ind₂ZrCl₂ and MAO (MAO/Zr = 400) kinetics observed in the various solvents, with and without activation, are compared in Figure 7. As may be seen, the catalytic activity is strongly improved by the preformation of the catalytic system. Since the amount of methylene dichloride used in the preactivation step correspond to about 5 to 7% of the total volume of the polymerization, the results cannot be simply explained by an increase of the polarity during the polymerization. For example, after activation in CH₂Cl₂, the polymerization activity observed in toluene is very close to the one found in pure methylene dichloride. More interesting in heptane, while the polymerization activity is almost null in absence of activation, preformation of the catalyst in a small volume of CH₂Cl₂, gives an activity relatively close to those found in other solvents.

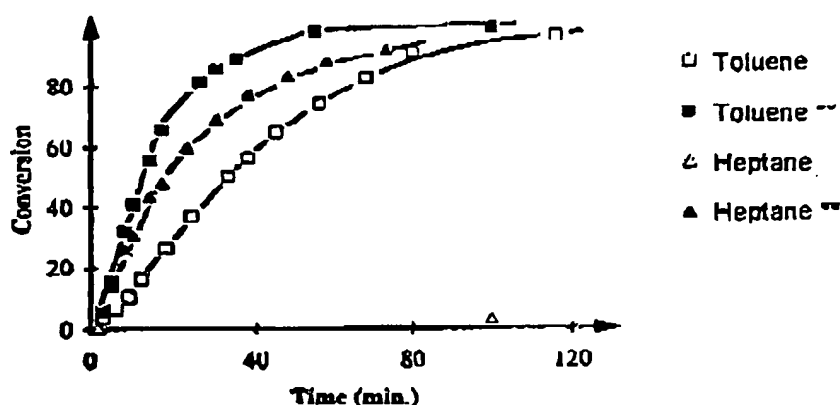


Figure 7: hex-1-ene conversion versus polymerization time, in various solvents : [Zr] = $5 \cdot 10^{-5}$ M ; MAO/Zr : 400 ; T = 20°C ; [Hex] = 1 M ; ** preformation of the catalyst in CH₂Cl₂

As may be seen in Figure 8, a linear relationship is still observed between the logarithm of monomer concentration and reaction time. Besides the first order monomer dependence of the polymerization, this indicates that the concentration of active species remains constant from the very beginning up to the almost complete hex-1-ene conversion. This strongly suggests, as already mentioned, that the catalytic active species are long-lived species, but also that once formed, their concentration is quite insensitive to the polymerization solvent, as shown by experiments made with catalyst preformation in CH₂Cl₂.

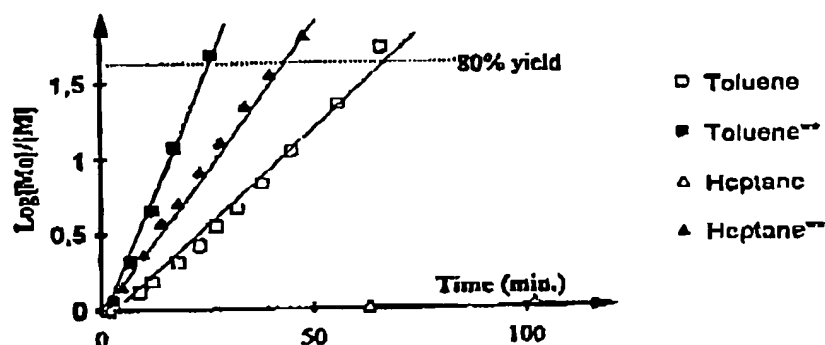


Figure 8: Semi-logarithmic variations of hex-1-ene consumption versus polymerization time, in various solvents : $[Zr] \sim 5 \cdot 10^{-5} \text{ M}$; MAO/Zr : 400 ; $T = 20^\circ\text{C}$; $[Hex] = 1 \text{ M}$; ** preformation of the catalyst in CH_2Cl_2

c) *Polymerization of ethylene with catalytic systems preformed in methylene dichloride*

In order to check if the results observed in the polymerization of hex-1-ene could be extended to the synthesis of other polyolefins, ethylene polymerization was investigated in the presence of *rac*-Et-Ind₂ZrCl₂/MAO ($MAO/Zr=400$) prepared in the polymerization solvent or preformed in CH_2Cl_2 . Preliminary data are collected in Table 1. As may be seen a pronounced effect of the conditions of catalyst formation is observed.

Table 1 : Influence of solvent and catalyst preformation on ethylene polymerization performed in the presence of *rac*-Et-Ind₂ZrCl₂/MAO ($MAO/Zr=400$). $T = 20^\circ\text{C}$; $P_{\text{eth}} = 5 \text{ bars}$; a) $MAO/Zr=800$.

Polymerization solvent	Catalyst preformation (solvent)	$10^6[Zr]$ (M)	Activity (Kg.Pol/moleZr.h)
Isododecane	no	4	~0
Toluene ^{a)}	no	1,3	4100
Dichloromethane	no	0,6	6700
Isododecane	toluene	2,9	2500
--	dichloromethane	2,6	4000

Owing to the known processes involved in the formation of active catalytic sites, the influence of reaction conditions, in particular the nature of the solvent, on the initial catalyst components, i.e., metallocene, methylaluminoxane and on the resulting cationic metallocene active species will be discussed.

References:

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Specific active or inactive catalysts

liquid quaternary catalyst

solvent